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RATE OF PRIMARY PHOTOPRODUCT FORMATION FOR AQUEOUS CR(EN)3(3+)--ETC(U)
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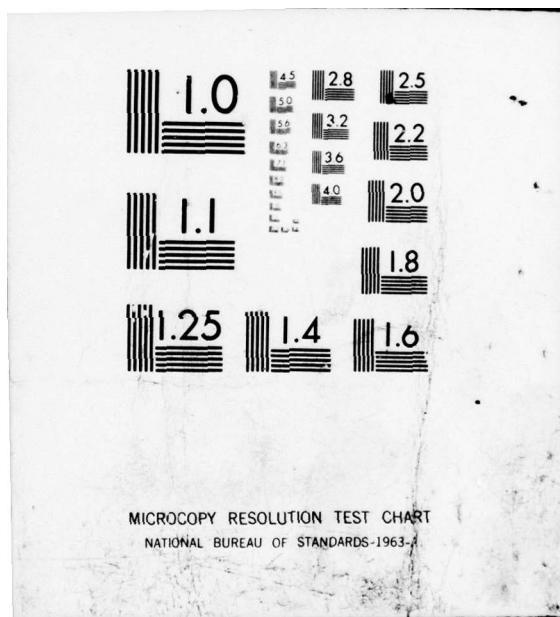
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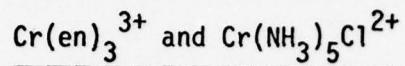
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20. Abstract (continued from previous page)

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Rate of Primary Photoproduct Formation for Aqueous



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Abstract

High energy pulsed laser photolysis at 530 nm shows that in the case of aqueous $\text{Cr}(\text{en})_3^{3+}$ there is both a prompt and a delayed appearance of primary photoproduct, $\text{Cr}(\text{en})_2(\text{enH})(\text{H}_2\text{O})^{4+}$ (B). The latter grows in with the lifetime of emission from the first double thexi state, D_1° . Analysis of the variation of the ratio of delayed to prompt absorbance change indicates that the first quartet thexi state, Q_1° , is formed with 70% efficiency and then reacts to give B with a yield of 0.17. D_1° is produced with 30% efficiency in a fast intersystem crossing, and then reacts to give B directly with a yield of close to unity. In the case of $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$, the primary photoreaction gives cis- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}^{2+}$ (AC). The appearance time is <5 nsec, too short to allow identification of the reacting excited state. The pK_a of AC is 6.2, and in neutral and alkaline solution the prompt absorbance change is followed by one of about 100 nsec grow-in time, identified as the rate of proton transfer from AC to the buffer base.

Introduction

Chromium(III) complexes have been the subject of many detailed photochemical and photophysical studies, ~~see Refs. 1-3.~~ The work described here has been addressed primarily to the possible resolution of an important uncertainty in the excited state reaction scheme. As shown schematically in Figure 1, absorption of light in the region of the first ligand field band yields a Franck-Condon (that is, vibrationally excited) excited quartet state, Q_{FC} . The thermally equilibrated excited or thexi state, Q_1° , is lower in energy and distorted in that bond length and bond angle changes relative to the ground state geometry likely have occurred. Prompt intersystem crossing, pic, to D_1° , may occur during thermal equilibration, where D_1° is the first doublet thexi state. The crossing may alternatively occur from Q_1° , and be called isc. D_1° may undergo back intersystem crossing, bisc, to Q_1° . Emission (phosphorescence) from D_1° is usually observable in room temperature, fluid solution, of lifetime τ_e . Chemical reaction to photoproducts may occur either from D_1° or Q_1° . The reaction may be the same as the thermal ground state reaction, or it may be different, in which case the photoreaction has been called antithermal.

An early supposition was that all Cr(III) photochemistry occurs from D_1° . With the appearance and experimental and theoretical authentication of the photolysis rules for Cr(III) complexes (see Refs. 1-3) many investigators went to the alternative conclusion that all photochemistry occurs from Q_1° . We retained, in this Laboratory, the specific caveat that possibly it was only antithermal type reactions that occurred from Q_1° , and that thermal ones might be occurring from D_1° .⁴ Later, quenching studies implicated D_1° in the photochemistry in that quantum yields, ϕ , were in some cases reduced on complete quenching of the emission. Reported

quenchable percents of ϕ are: $\text{trans-Cr}(\text{NH}_3)_2(\text{NCS})_4^-$, 60% (in a low temperature solvent)⁵; $\text{Cr}(\text{en})_3^{3+}$ (en = ethlenediamine), 35-60% (depending on quencher and excitation wavelength)⁶⁻⁸; $\text{trans-Cr}(\text{en})_2(\text{NCS})_2^+$, 80%⁹; $\text{Cr}(\text{bipyridine})_3^{3+}$, 100%¹⁰; $\text{Cr}(\text{CN})_6^{3-}$, 0% (see Ref. 2). The unquenchable portion of ϕ must come from directly formed Q_1° , but the quenchable fraction could in general be due either to reaction from D_1° or from Q_1° produced by bsc. The latter conclusion was advanced in the cases of $\text{Cr}(\text{en})_3^{3+}$ and $\text{trans-Cr}(\text{en})_2(\text{NCS})_2^+$, and the former, in that of $\text{Cr}(\text{bipy})_3^{3+}$ (bipy = 2,2'-bipyridine). More recently, it has been proposed that in all cases the quenchable reaction occurs from D_1° .^{11,12} The identification of the reactive thexi state is thus a matter of much current discussion. Lifetimes of Q_1° states under photochemical conditions are also uncertain, only indirect estimates having been possible.

The nature of the intersystem crossing process is also under debate. Excited state absorption, ESA, of D_1° appears within short psec in the cases of $\text{Cr}(\text{NCS})_6^{3-}$, $\text{trans-Cr}(\text{NH}_3)_2(\text{NCS})_4^-$, and $\text{trans-Cr}(\text{en})_2(\text{NCS})_2^{+1}$,¹³ but the path could be either psc or isc.

The above questions are ones addressed by the present investigation. The approach is to determine the rate of primary photoproduct formation by monitoring absorbance changes following pulsed laser photolysis under conditions such that significant ground state bleaching occurs. In a preliminary report,¹⁴ such monitoring experiments showed a prompt and a delayed appearance of photoproduct in the case of aqueous $\text{Cr}(\text{en})_3^{3+}$, the latter having a grow-in time the same as τ_e . We concluded that 66-69% of the photoreaction occurred through D_1° , in approximate agreement with the quenching results. The corroboration is not trivial, however. In quenching experiments there is the possibility that quenching encounters are not "innocent"¹⁵ with respect to inducing chemical reaction.

The present paper extends the results with $\text{Cr}(\text{en})_3^{3+}$ and adds data for a new complex, $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$. This last was chosen because the dominant photoreaction is antithermal (aqueous of the trans ammonia see Ref. 1) and, according to present thinking, should occur from Q_1° .

Experimental Section

Materials. $[\text{Cr}(\text{en})_3](\text{ClO}_4)_3$. The chloride salt was prepared according to a literature procedure,¹⁶ and the corresponding perchlorate salt, by the dropwise addition of concentrated perchloric acid to a cooled aqueous solution. The product was recrystallized at 5°C. Its aqueous solution absorption spectrum agreed within experimental error (3-5%) with that reported.¹⁷

$[\text{Cr}(\text{NH}_3)_5\text{Cl}](\text{NO}_3)_2$. The chloride salt (Alfa Inorganics) was converted to the nitrate by recrystallization from several molal aqueous potassium nitrate, and recrystallized from dilute aqueous potassium nitrate. A 10^{-2} M HClO_4 solution of the dark red crystalline product gave an absorption spectrum agreeing with that in the literature.¹⁷

$[\text{Cis-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$. This compound was prepared according to a literature protocol,¹⁸ and again gave satisfactory agreement with a published absorption spectrum.¹⁹

Lutidine (2,6-dimethylpyridine) and collidine (2,4,6-trimethylpyridine) were obtained from Tridom Chemicals, Inc., Hauppauge, New York, and were distilled prior to use. Chemicals were of reagent grade; the deionized water used was pure in the sense that laser pulse flashing produced no monitoring artifacts.

Photolysis equipment and procedures. - Aspects of the laser photolysis apparatus have been described previously,¹¹ and the block diagram for the equipment is shown in Fig. 2. We used 530 nm pulses of about 1 J and 0.5 J energy for the $\text{Cr}(\text{en})_3^{3+}$ and $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$ systems, respectively. The working measurement of pulse energy was by means of the photodiode pulse, recorded as one of the oscilloscope traces. This photodiode output was calibrated by means of a Korad Model 108 ballistic thermopile.

The photodiode trace allowed correction of the monitoring results for the $\pm 10\%$ variation in laser pulse energy.

The one cm diameter laser beam was shaped with a cylindrical lens (15 cm focal length) to give an irradiated area of 2x9.5 mm on the front window of a four clear sided pyrex fluorescence cell. The monitoring light was provided by a 1000 W Hanovia Xe arc lamp, and was collimated and defined by slits so that a 2x2 mm beam passed through the irradiation cell at a right angle to the photolyzing laser pulse, and about 1/2 mm from the front (laser side) window of the cell. The monitored volume was thus 2x2x9.5 mm³. The cell itself was in a cell holder whose temperature (and that of the solution in the cell) was controlled to 0.1°C by circulating thermostatted water.

The transmitted monitoring beam was partially focussed down onto the entrance slit of the Oriel monochromator¹¹ (with preceding filters to cut out scattered 530 nm light), and exited onto a 5 stage RCA 4840 photomultiplier (PMT).²⁰ The output current never exceeded 3 mA in an experiment, and the system rise and fall time was < 3 nsec. In obtaining this performance, we avoided saturation effects by limiting the on-time of the monitoring light to about 2 msec by means of a Vincent Associates mechanical shutter. The sequencing was that triggering first opened the shutter, followed by the laser pulse. The PMT output was dropped across the 50 ohm input terminal of the 7A19 amplifier with a 7B92 time base in a Tektronix 7844 chassis. The dual beam trace of the oscilloscope was recorded by means of a Model C-51 camera.

Emission lifetimes were measured as previously described,¹¹ except that the five stage PMT was used in the case of Cr(NH₃)₅Cl²⁺. Corning glass filters were placed on the monochromator entrance slit in order to block out the 530 nm laser light, but transmit at greater than 600 nm.

Sample handling was as follows. Solutions were made up to have optical densities of about unity per cm at 530 nm, so that concentrations were about 0.2 M for $\text{Cr}(\text{en})_3^{3+}$ (and 0.01 M in HClO_4) and 0.03 M for $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$. They were filtered immediately before use through a 0.22μ Millipore filter (twice filtered in the case of $\text{Cr}(\text{en})_3^{3+}$ solutions): this was essential, to avoid artifacts in the monitoring traces (note Ref. 21). Solutions were freshly prepared for each set of runs; since the irradiation cell contained about 2.5 cm^3 , or much more than the monitored volume, the mixing between successive experiments allowed several (never more than ten) photolyses to be carried out with each filling. All measurements were with air equilibrated solutions and, except for temperature dependence studies, were at 20°C in the case of $\text{Cr}(\text{en})_3^{3+}$ and 17°C in that of $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$. Absorption spectra were measured by means of a Beckman Acta MVI spectrophotometer; the absorption at 530 nm and at the monitoring wavelengths to be used were determined just before each set of runs, and occasionally afterwards as a check that the overall extent of reaction was negligible.

Detailed absorption spectra. - Analysis of the monitoring results required accurate values of γ , the ratio of extinction coefficients of the initial complex to that of the primary photoproduct, including wavelength regions of weak absorption. We thus needed measurements at more than the usually emphasized absorption band maxima positions. As in the photolyses, all solutions were Millipore filtered before use.

In the case of $\text{Cr}(\text{en})_3^{3+}$ (A), the primary photoproduct is $\text{Cr}(\text{en})_2(\text{enH})(\text{H}_2\text{O})^{4+}$ (B).^{22,23} We determined the absorption spectrum of B as follows. A solution of A, acidified to pH 2 with perchloric acid, was photolyzed at 515 nm to successive small degrees by means of an Ar ion laser. The degree of photolysis was determined from the absorbance

changes around 450 nm, using extinction coefficients, ϵ_B , reported in the literature.²⁴ We could then calculate ϵ_B for wavelengths where the literature values are not clear or not reported. The resulting spectrum is shown in Fig. 3. (Species B aquates to the final product, cis-Cr(en)₂(H₂O)₂³⁺, sufficiently slowly that spectral drifts following photolysis could be allowed for).

The same spectrum was obtained directly. Low temperature (5°C) Sephadex chromatography of a photolyzed solution yield B as an orange fraction. Chromium analysis allowed the absorption spectrum to be converted to an extinction coefficient scale, and we find the reported²⁴ value of 55 M⁻¹ cm⁻¹ at the first ligand field band maximum and of 3.3 M⁻¹ cm⁻¹ at our most common monitoring wavelength of 580 nm.

In the case of Cr(NH₃)₅Cl²⁺ (C), the dominant photoproduct is cis-Cr(NH₃)₄(H₂O)Cl²⁺^{1,2} (AC). The absorption spectrum of the latter complex changes in alkaline solution because of conversion to cis-Cr(NH₃)₄(OH)Cl⁺ (HC). The set of spectra is given in Fig. 4.

Determination of the absorption spectrum of HC was complicated by reaction, presumably chloride aquation, at pH's above, about 6. Thus at pH 8.6 (and 17°C), the absorbance at 580 nm decayed (to a low terminal value) with a rate constant of 6.33x10⁻³ sec⁻¹. A directly obtained absorption spectrum at a sufficiently high pH that only HC would be present would have been subject to large and therefor inaccurate correction for this chloride aquation. An indirect procedure was therefor used.

We first determined the pK_a of AC by titration. Equal volumes of ionic strength 0.2 buffer and 8x10⁻³ M AC were mixed and the absorbance measured at 580 nm, correcting for drift where necessary. This was done for several pH's, the buffers being (pH range, buffer): (5.2-5.5, acetate), 5.9-6.3, 2,6-lutidine), (6.5-8.0, 2,4,6-collidine), (>8, ammonia). Ammine

type buffers were used because of indications of ion pairing effects with phosphate buffers. The degree of neutralization of the weak acid AC is given by

$$F = \frac{(HC)}{(AC) + (HC)} = \frac{K_a}{K_a + (H^+)} = \frac{D_{pH} - D_{acid}}{D_{base} - D_{acid}} \quad (1)$$

where K_a is the acid dissociation constant of the aquo-chloro complex, and the D's denote optical density at a given pH, in acidic, and in basic solution. The results are shown in Fig. 5, where the solid line is F calculated for $pK_a = 6.25$, and agrees reasonably with the data. Such a pK_a value is in the range found for coordinated water.^{25,26}

The complete absorption spectrum for the hydroxy-chloro complex, HC, was then calculated from that for a solution at pH 5.8 and the known value of F. At this pH the drift due to secondary reaction was slow enough that an accurate spectrum could be obtained.

We also confirmed that the spectral change on photolysis of a pH 1 solution of $Cr(NH_3)_5Cl^{2+}$ corresponded to the formation of AC. Also, on making the photolyzed solution basic, the absorption spectrum changed as expected for the formation of HC, and on re-acidifying, the absorption spectrum returned to that immediately after photolysis.

Results

Cr(en)₃³⁺. A typical pair of oscilloscope traces is given in Ref. 14. At 580 nm, for example, there is a prompt absorbance increase, that is, one which parallels the integrated 20 nsec laser pulse, followed by a slower absorbance increase with a grow-in time of around 1 μ sec, depending on the temperature. No further change occurred up to the longest time monitored, about 200 μ sec. As previously reported,¹⁴ the grow-in is exponential, that is, of the form $(D_{\infty} - D_t) / (D_{\infty} - D_{in}) = \exp(-t/\tau_p)$, where τ_p is the grow-in time, D_t is the absorbance at time t following the pulse, D_{∞} , the value after no further change, and D_{in} , the value immediately after the laser pulse. Further, the τ_p and τ_e values at various temperatures agreed well.

The total absorbance change, $(D_{\infty} - D_0)$, where D_0 is the value before arrival of the laser pulse, agreed with that calculated from the energy of the laser pulse, the quantum yield for photolysis, and the values of ϵ_A and ϵ_B . The ca. 20% uncertainty in this comparison resided mainly in the difficulty of estimating with any accuracy the number of photolyzing quanta absorbed in the volume seen by the monitoring beam. However, within this uncertainty, the agreement between observed and calculated absorbance changes held over a range of wavelengths. We therefor identify the photoproduct seen on the monitoring time scale as indeed species B, or the same as observed in ordinary photolyses.

Our monitoring results are reported as R , the ratio of delayed to prompt absorbance change, $R = (D_{\infty} - D_{in}) / (D_{in} - D_0)$. Figure 6 shows the variation of R (and of γ) with wavelength of the region 540-620 nm. The R value at 620 nm was the most subject to error. Absorbances are small at this wavelength and the precision of reading the optical density changes was noticeably reduced.

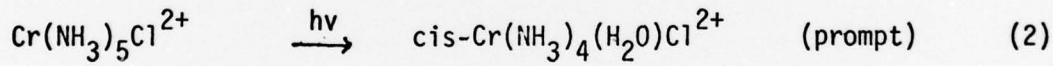
It was of interest to determine whether emission quenchers also quenched the slow absorbance grow-in. Substantial quenching is reported for solutions > 1 M in Co(II) or Fe(II),⁶ and for ones 0.01 - 0.1 M in hydroxide.⁷ However, the monitoring traces obtained on laser pulse photolysis of such systems were complex in nature, with non-exponential growths or decays in absorbance, and on time scales unrelated to the D_1° emission lifetime. Several types of experiments were carried out with alkaline solutions. There is complete emission quenching in 0.1 M sodium hydroxide (and 0.25 M $\text{Cr}(\text{en})_3^{3+}$), as reported.⁷ The monitoring traces changed on sequential flashing, however. In a second series, the solution was 0.002 M in hydroxide and 0.09 M in complex, and was prepared with boiled water, nitrogen degassed, and sealed against exposure to air, to avoid any pH change due to absorption of atmospheric carbon dioxide. The emission lifetime was about 60 nsec, but lengthened and became complex on sequential flashing. There was still a possibility of carbonate impurity in the reagent sodium hydroxide, and we felt that the effect of carbonate ion should be investigated directly. For this reason, and to minimize any pH change due to photolysis, some experiments were made with a carbonate buffer at a pH such that hydroxide quenching was negligible. A solution 0.02 formal each in sodium carbonate and bicarbonate showed a pH of 10.05, but on making the solution 0.09 formal in complex, the pH dropped to 9.4. The effect could be due to displacement of the carbonate hydrolysis equilibrium by ion pairing with the complex. The emission lifetime for this solution was ≈ 40 nsec, and since the complex was in excess, there must have been dynamic as well as possible static quenching. Similarly, for a solution 0.005 formal in carbonate and in bicarbonate, but at essentially the same pH and complex concentration, the emission lifetime was 130 nsec. By comparison, the lifetime for the complex

in a pH 9.4 solution with no added carbonate or bicarbonate was virtually the unquenched value (1.7 μ sec at 21°C).

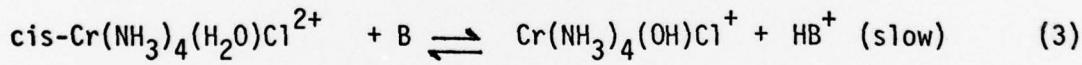
Because of the number and complexity of these various effects, they were not pursued in detail. It does seem clear that chemical events more complicated than simple hydroxide quenching were occurring, and ones which made unreliable any conclusions from the monitoring traces about the extent of primary photoproduct formation or its appearance rate.

$\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$. The initial experiments were carried out with unbuffered solutions of $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$ at their natural pH of about 6. Monitoring at 580 nm showed a prompt absorbance increase, and a slow one with a grow-in time of long nsec. However, in acidic solutions only the prompt absorbance increase was present. Monitoring experiments were then carried out in solutions buffered at various pH's.

To anticipate the discussion, we identify the prompt and slow absorbance changes as due to the respective processes:



C AC



AC HC

where B and HB^+ are the buffer base and acid species, respectively. The hydroxy-chloro complex, HC, is probably the cis isomer, but this was not determined. In acidic media, the total absorbance change in a monitoring experiment, $(D_\infty - D_0)$, should be proportional to the extinction coefficient difference $(\epsilon_{\text{AC}} - \epsilon_{\text{C}})$, while in basic media, the change should be determined by $(\epsilon_{\text{HC}} - \epsilon_{\text{C}})$. That this is essentially the case is shown in Fig. 7.

First, the variation of the total absorbance change on pulse photolysis of a pH 2 solution closely parallels that of $(\epsilon_{AC} - \epsilon_C)$, except at the shortest wavelengths. Further, as shown in Fig. 7b, $[(D_\infty - D_0)_{base} - (D_\infty - D_0)_{acid}]$ closely parallels the variation in $[\epsilon_{HC} - \epsilon_{AC}]$, again with deviation setting in at the shortest wavelengths. This deviation is discussed further below; the rest of the spectral agreements are satisfactory.

A second test of the correctness of reactions (2) and (3) consisted of a series of laser pulse photolyses in variously buffered solutions. If the final product is the equilibrium mixture of AC and HC species, then

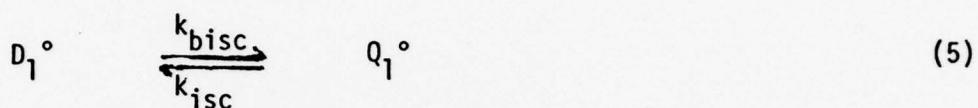
$$F = \frac{(D_\infty - D_0)_{pH} - (D_\infty - D_0)_{acid}}{(D_\infty - D_0)_{base} - (D_\infty - D_0)_{acid}} = \frac{K_a}{K_a + (H^+)} \quad (4)$$

Subscripts acid and base are for data at a sufficiently low and sufficiently high pH, respectively, that the photoproduct was entirely in the AC and HC forms respectively. The values of F obtained from the monitoring data at 580 nm are included in Fig. 5. These values were always corrected for any small variations in the laser pulse energy, as determined by the photodiode trace.

In alkaline solutions, where it was most apparent, the grow-in of the slow absorbance increase at 580 nm was exponential. That is, the equation $[(D_t - D_\infty) / (D_{in} - D_\infty)] = \exp. (-kt)$ was obeyed. The grow-in time, $1/k$, was 100-130 nsec for a solution at the natural pH and ranged downward in buffered solutions, depending on the buffer and its concentration. These variations were not explored in any detail.

Discussion

$\text{Cr}(\text{en})_3^{3+}$. The various processes to be considered, shown in Fig. 1, were described in the Introduction. Those involving D_1° or Q_1° as reactant can be considered as ordinary thermal reactions obeying, for example, transition state rate theory; D_1° and Q_1° are postulated to be good thermodynamic species.²⁷ The reaction



is essentially one of isomerization, albeit with a spin change. Also, the quantity f_{isc} can be written as a ratio of rate constants. However, f_{pisc} is merely a branching ratio during thermal equilibration.

We can, for the moment, avoid any assumption as to the relative importance of pisc vs. isc as the route whereby D_1° is formed, and as to whether product, B, is produced by direct reaction from D_1° , or results from bisc and reaction from Q_1° . The kinetic analysis of the monitoring experiment is as follows. Before the laser pulse, there is concentration $(A)_0$ of complex and, approximating the monitoring beam path length as 1 cm, optical density $D_0 = (A)_0 \epsilon_A$. Immediately after the laser pulse, we have $D_{\text{in}} = (A)_{\text{in}} \epsilon_A + (D_1^\circ)_{\text{in}} \epsilon_D + (B)_{\text{in}} \epsilon_B$, where ϵ_D is the extinction coefficient for ESA (by D_1°). We assume that intersystem crossing is prompt, so that $(D_1^\circ)_{\text{in}} = f I_a$ where I_a denotes the moles per liter of light quanta absorbed by A from the laser pulse, in the volume monitored. The prompt product formation is assigned to a fast reaction from directly formed Q_1° , $(B)_{\text{in}} = I_a (1 - f) \phi'_Q$, where ϕ'_Q is the fraction of Q_1° exiting by chemical reaction to photoproduct. Finally, $(A)_{\text{in}} = (A)_0 - I_a + I_a (1 - f) (1 - \phi'_Q)$.

At long times, that is, after the complete grow-in of the slow absorbance change, $D_\infty = (A)_\infty \epsilon_A + (B)_\infty \epsilon_B$, where $(A)_\infty = (A)_0 - I_a + I_a(1 - f)(1 - \phi'_Q) + I_a f(1 - \phi'_D)$ and $(B)_\infty = I_a(1 - f)\phi'_Q + I_a f\phi'_D$; ϕ'_D is the fraction of D_1° that exits by chemical reaction to photoproduct. From emission studies, $(D_1^\circ) = (D_1^\circ)_{in} \exp(-t/\tau_e)$ algebraic manipulation shows that $(D_t - D_\infty)/(D_{in} - D_\infty) = \exp(-t/\tau_p)$, $\tau_p = \tau_e$. That is, the slow absorbance change should grow in with the same lifetime. That this is what is observed is a confirmation of the general correctness of the reaction scheme.

Further manipulation of the above relationships gives

$$R = \frac{D_\infty - D_{in}}{D_{in} - D_0} = \frac{\phi_D(\gamma - 1) + f(1 - \delta)}{\phi_Q(\gamma - 1) - f(1 - \delta)} \quad (6)$$

where $\phi_D = f\phi'_D$ and is that portion of the overall quantum yield due to reaction form or through D_1° ; similarly, $\phi_Q = (1 - f)\phi'_Q$, and is the yield due to reaction from directly formed Q_1° . Also, $\phi = \phi_D + \phi_Q$. The quantities γ and δ are the extinction coefficient ratios ϵ_B/ϵ_A and ϵ_D/ϵ_A , respectively; δ is zero if there is no ESA. If γ is large compared to unity (or to δ , if $\delta > 1$), the Eq. (6) reduces to $R = \phi_D/\phi_Q$.

Our results are shown in Fig. 6. In the wavelength region 580 - 610 nm, γ is large and R should be independent of wavelength, as observed. We discount the importance of δ for two reasons. First, δ should vary with wavelength, and were it large, such variation should make R wavelength dependent, contrary to observation. Second, were δ large, I_a would not be proportional to the laser pulse energy, and neither would the monitored absorbance changes. No such dependence on pulse energy was observed over about a two fold variation.

The increase in R at 620 nm is expected since γ is now small enough that the f terms in Eq. (6) cannot be neglected. The solid line in Fig. 6 is calculated for $f = 0.3$, $\phi_D' = 0.88$, and $\phi_Q' = 0.15$, assuming the literature value of 0.37 for ϕ (see Ref. 1). We conclude that in the wavelength region 580 - 620 nm, δ is not important, and that the above parameters describe the photochemistry. The relatively precise R values at around 580 - 600 nm give ϕ_D and ϕ_Q as 0.26 and 0.11, respectively, to about 5% relative error. Although larger, the error limits in R at 620 nm still place f as 0.33 ± 0.09 . We can thus conclude that the range of ϕ_D' is between 0.64 and 1.00 or 0.8 ± 0.2 and that of ϕ_Q' , between 0.14 and 0.19, or 0.17 ± 0.03 .

The ratio ϕ_D/ϕ of 0.70 ± 0.03 is somewhat higher than that found in quenching studies but, within our error limits, should be the more reliable. For example, if quenching encounters induce chemical reaction, too low a quenchable yield will be reported. This could be true in the case of OH^- as quencher, where for around 530 nm irradiation only about 35% quenchable photolysis is reported.⁷ There are, in addition, the chemical complexities suggested by our monitoring and emission results. The 60% quenchable photolysis found for Co(II) and Fe(II) as quenchers (and with shorter wavelength irradiation)⁶ could be in error either because of non-innocent quenching or because the high quencher concentrations needed (> 1M) in effect altered the nature of the medium.

The present results answer in part the questions posed in the Introduction. First, we have by direct measurement provided an upper limit to the lifetime of Q_1° ; $\tau(Q_1^\circ) \leq 3$ nsec in view of the closeness with which the prompt absorbance increase follows the integrated laser pulse. Second, the path of bisection and reaction from Q_1° cannot be important. This

path requires that ϕ'_D be $\leq \phi'_Q$. That is, the efficiency for no path for chemical reaction to products that passes through Q_1° can exceed the efficiency of reaction from Q_1° itself. Allowing for our error limits, the majority path for disappearance of D_1° is that of direct chemical reaction; this conclusion is confirmed by the quantitative considerations that follows. We thus rule out bisc as a reaction of major importance.

This same conclusion was arrived at on a more general basis, from emission studies.¹² Emission rules for Cr(III) complexes were proposed:

Rule 1: For complexes with six equivalent Cr-L bonds, the emission lifetime in room temperature fluid solution decreases with decreasing ligand field strength.

Rule 2: If two different kinds of ligands are coordinated, the emission lifetime will be relatively short if that ligand which is preferentially substituted in the thermal reaction lies on the weak field axis of the complex.

A rationale for these rules is that thermal (as opposed to antithermal) photochemistry likely occurs from D_1° . In related studies,¹¹ it was specifically proposed that the emission lifetime of Cr(III) complexes in fluid solution is determined by the rate of chemical reaction from D_1° rather than by non-radiative relaxation to the ground state or by the bisc rate. Our results confirm this proposal in the case of $\text{Cr}(\text{en})_3^{3+}$; the emission lifetime is mainly determined by the rate of chemical reaction of D_1° to photoproduct, $k_{\text{cr}} = 5.4 \times 10^5 \text{ sec}^{-1}$ at 20°C .^{12,28} The temperature dependence of the emission lifetime, and hence of k_{cr} , gives the frequency factor A_{cr} , $A_{\text{cr}} = 5.4 \times 10^5 \exp(10,000/293 \text{ R}) = 1.6 \times 10^{13} \text{ sec}^{-1}$. This is in the normal range of values.

We are not able to give a definitive answer to the question of whether the f value of 0.3 should be attributed to pisc or to isc. If the latter is the case, some rate constant analysis is possible, however. Referring

to Fig. 1, we know that $(k'_{nr} + k'_{cr} + k'_{isc}) \geq 3 \times 10^8 \text{ sec}^{-1}$ since the prompt product formation occurs within the time of the laser pulse. Further, since f_{isc} is now assigned as 0.3, $(k'_{nr} + k'_{cr}) \approx 2.3 k'_{isc}$, whence $k'_{isc} \geq (0.9) \times 10^8 \text{ sec}^{-1}$. In fact, by using a 5 nsec excitation pulse, we can state from the closeness with which the rise in emission intensity follows laser pulse, that $k'_{isc} \geq 1 \times 10^9 \text{ sec}^{-1}$. Further, since $\phi'_Q \approx 0.17$, $(k'_{nr} + k'_{isc}) = 4.9 k'_{cr}$, so that $k'_{cr} = (0.56) k'_{isc} \geq 0.5 \times 10^8 \text{ sec}^{-1}$. Since $k_{bisc} \leq 10.6 \text{ sec}^{-1}$ (no greater than $1/\tau$ and much less if ϕ'_D is close to unity), K for Eq. 5 is: $K_5 = k_{bisc}/k'_{isc} \leq 0.02$.

We also have an estimate for E_{isc}^* . In emission studies, extrapolation of the emission decay to time zero after the laser pulse gives an initial oscilloscope reading V_0 which is proportional to I_0 , the initial emission intensity, which in turn is proportional to $f k_r$. Since k_r should not be temperature dependent, that of V_0 should be due to f . For Cr(en)_3^{3+} , this corresponds to an apparent activation energy of $4.5 \text{ kcal mole}^{-1}$,¹² which we now assign as E_{isc}^* . The quantity $\exp(-E_{isc}^*/RT)$ is 5×10^{-4} at 25° C , so the frequency factor for k_{isc} becomes $A_{isc} \geq 2 \times 10^{12} \text{ sec}^{-1}$. The lower limit is within the range of normal values for a unimolecular reaction. The actual value of k_{isc} should perhaps be taken to be near its lower limit, or $\sim 1 \times 10^9 \text{ sec}^{-1}$. This is a rather smaller value than that obtained from the appearance time of excited state absorption in other Cr(III) complexes.¹³ These were thiocyanate containing complexes, however, and for two of them, $\text{trans-Cr(en)}_2(\text{NCS})_2^+$ and $\text{trans-Cr(NH}_3)_2(\text{NCS})_4^-$, the respective temperature dependencies of V_0 are known, and correspond to E_{isc}^* values of 0.0 and $-2.3 \text{ kcal mole}^{-1}$. For the same A_{isc} , k_{isc} should indeed be powers of ten faster than for Cr(en)_3^{3+} .

Returning to the 4.5 kcal mole⁻¹ value for E_{isc}^* , the energy gap ($Q_1^\circ - D_1^\circ$) has been estimated to be about 14 kcal mole⁻¹ (Ref. 7 and citations therein), so that E_{bisc}^* becomes about 18.5 kcal mole⁻¹. Since $E_{cr}^*(D_1^\circ)$ is only 10 kcal mole⁻¹, it would not be surprising that k_{cr} be much greater than k_{bisc} . Our results thus generate no major inconsistencies if f is identified as f_{isc} .

The alternative interpretation, $f = f_{pisc}$, allows less numerical elaboration. E_{pisc}^* is now 4.5 kcal mole⁻¹, attributed to solvation shell effects on the thermal equilibration escape probability of Q_{FC} .¹² We now neglect k_{isc} and conclude that $k_{cr}' \geq 6 \times 10^7$ sec⁻¹ and $k_{nr}' \geq 3 \times 10^8$ sec⁻¹. These are permissible ranges, so again there is no inconsistency. There is evidence, which we accept, that D_1° appears via $pisc$ rather than by isc .²⁹ Note that by this interpretation, k_{bisc} should again be small compared to k_{cr} .

Returning to Fig. 6, R deviates from the calculated values, in the case of wavelengths **less** than 580 nm. The deviations are in the direction expected if ESA is becoming important, and the calculated δ values are included in the figure. In more detail, we have, (wavelength, nm; δ ; ϵ^*): (580; 1.2; 0.1), (570; 4.0; 0.57), (560; 3.9; 1.36). Here, ϵ^* is the extinction coefficient for the ESA, in $M^{-1}cm^{-1}$. Qualitatively, it appears that we are observing the long wavelength tail of the first D_1° absorption band, a band that possibly resembles the first ligand field bands of $Cr(en)_3^{3+}$ and of photoproduct and lies between them (see Fig. 3).

$Cr(NH_3)_5Cl^{2+}$. As noted in the Introduction, this complex was chosen because the principal photoreaction, being antithermal, probably occurs from Q_1° ; it is also a well studied system in terms of ordinary photochemistry. Initial results were exciting in that both a prompt and a slow absorbance change were observed. From emission studies, the lifetime of D_1° is

< 5 nsec,¹² and it appeared that the slow grow-in might be giving the Q_1° lifetime. However, as detailed in the preceding section, the pH dependence of the monitoring results seems to establish the reaction sequence (2) and (3). The slow absorbance change is due to reaction (3). The formation of primary photoproduct, AC, is too short for us to measure and we therefor cannot state whether or not it corresponds to the D_1° lifetime. We believe, however, that the reacting state is Q_1° , whose lifetime must therefor be < 5 nsec.

It is worth noting that the monitoring results indicate that the primary photoproduct is the aquo-chloro complex, AC, at all pH's, including ones such that the hydroxy-chloro species, HC, is the thermodynamically preferred form. The inference is that the lifetime of the reactive excited state is too short for encounters with a base to be important, the photo-reaction involving already present, that is, solvation shell water.

We have written Eq. (3) as involving a general base B, rather than OH^- ion. The grow-in time of the slow absorbance increase at 580 nm is about 100 nsec in the pH range 6 - 8. Were reaction (3) written with OH^- ion as the reactant, the bimolecular rate constant would greatly exceed the diffusion rate limit. It is for this reason that we suppose the solvent buffer base, B, to be the reactant.

It was noted in the preceding section that the monitoring results departed measurably from expectation at the shorter wavelengths studied. We are not sure of the explanation. High energy pulsed laser conditions are relatively drastic, however, and it is possible that some decomposition products are formed, whose absorption becomes noticeable in the near uv. Recalling the indication of ESA in the case of $\text{Cr}(\text{en})_3^{3+}$, there is, for example, the possibility that some such occurred here, to give small amounts of redox decomposition and ensuing polymeric species.

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(28) Literature values for $\text{Cr}(\text{en})_3^{3+}$ are 1.33 μsec at $\sim 20^\circ\text{C}$ ⁶ and 1.85 μsec at 20°C .¹²

(29) See Refs. 7, 13, and 11. Note also Refs. 8 and 30.

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Legends for the Figures

Figure 1. Excited state scheme for a d^3 system.

Figure 2. Block diagram of the laser and monitoring equipment.

Figure 3. Absorption spectra for aqueous $\text{Cr}(\text{en})_3^{3+}$ (solid line) and $\text{Cr}(\text{en})_2(\text{enH})(\text{H}_2\text{O})^{4+}$ (dashed line).

Figure 4. Absorption spectra for aqueous $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$ (solid line), $\text{cis-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}^{2+}$ (dashed line), and $\text{Cr}(\text{NH}_3)_4(\text{OH})\text{Cl}^+$ (dot-dashed line).

Figure 5. \textcircled{O} : Variation with pH of $(D_{\text{pH}} - D_{\text{acid}})/(D_{\text{base}} - D_{\text{acid}})$ from spectrophotometric studies of aqueous $\text{cis-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}^{2+}$. $\textcircled{\bullet}$:

Variation with pH of total absorbance change, following laser pulse photolysis of $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$ at 530 nm, plotted as $[D_0 - D_{\infty}]_{\text{pH}} - (D_0 - D_{\infty})_{\text{acid}}/[[(D_0 - D_{\infty})_{\text{base}} - (D_0 - D_{\infty})_{\text{acid}}]$.

Figure 6. Primary photoproduct formation on 530 nm pulse photolysis of aqueous $\text{Cr}(\text{en})_3^{3+}$. $\textcircled{\bullet}$: Experimental R values (numbers in parentheses give the number of experiments). \textcircled{O} : Variation of γ with wavelength (with smoothing line). Full line: R calculated for $\delta = 0$.

Figure 7. (a) Plot of $\Delta = (\epsilon_{\text{AC}} - \epsilon_{\text{C}})$ versus wavelength, solid line, left abscissa scale. Points with error bars are for $\Delta' = (D_{\infty} - D_0)_{\text{acid}}$ from monitoring experiments, right abscissa scale.

(b) Plot of $\Delta = (\epsilon_{\text{HC}} - \epsilon_{\text{AC}})$ versus wavelength, full line, left abscissa scale. Points with error bars are for $\Delta' = [(D_{\infty} - D_0)_{\text{base}} - (D_{\infty} - D_0)_{\text{acid}}]$ from monitoring experiments, right abscissa scale.

Fig. 1

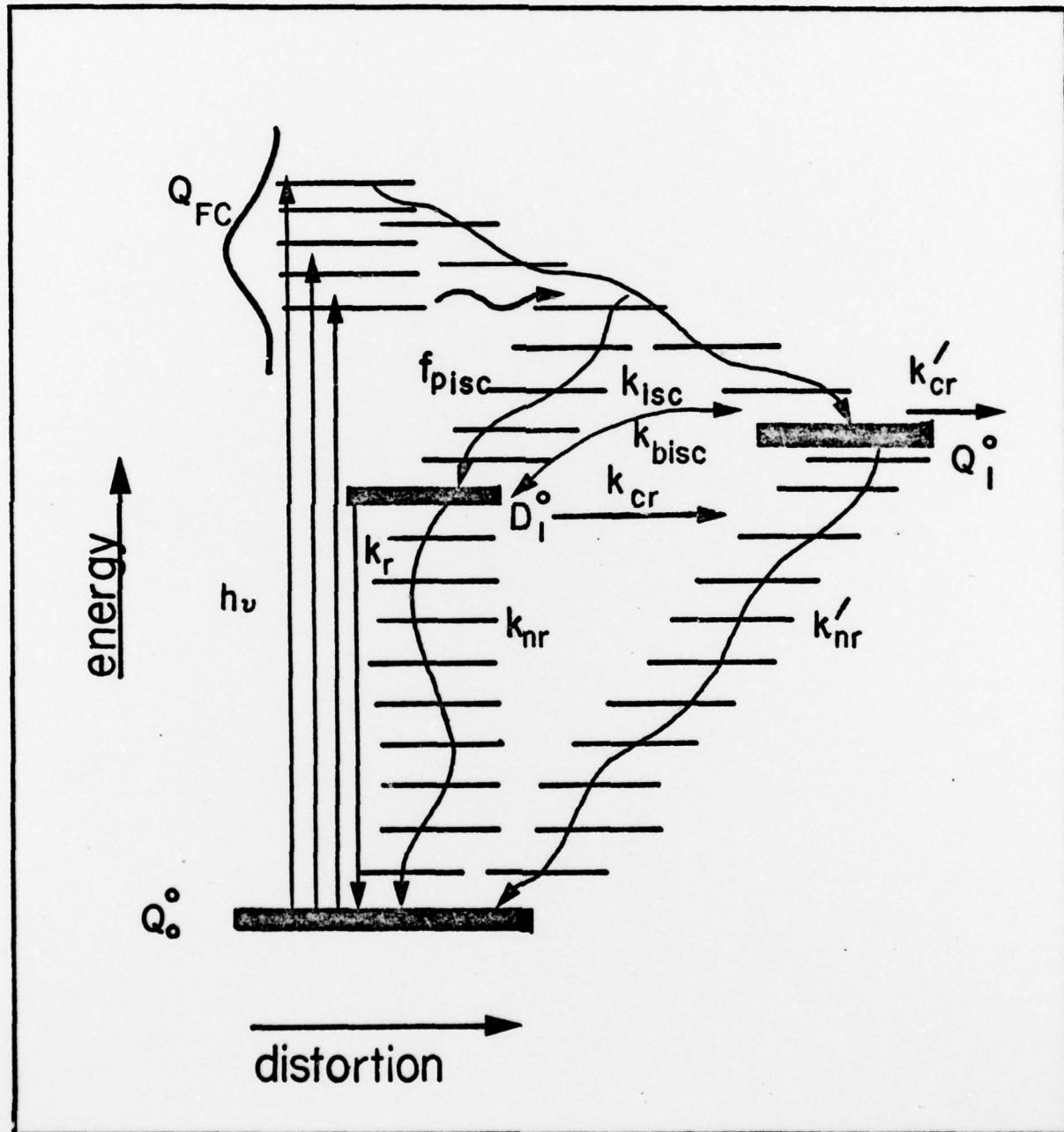


Fig 2

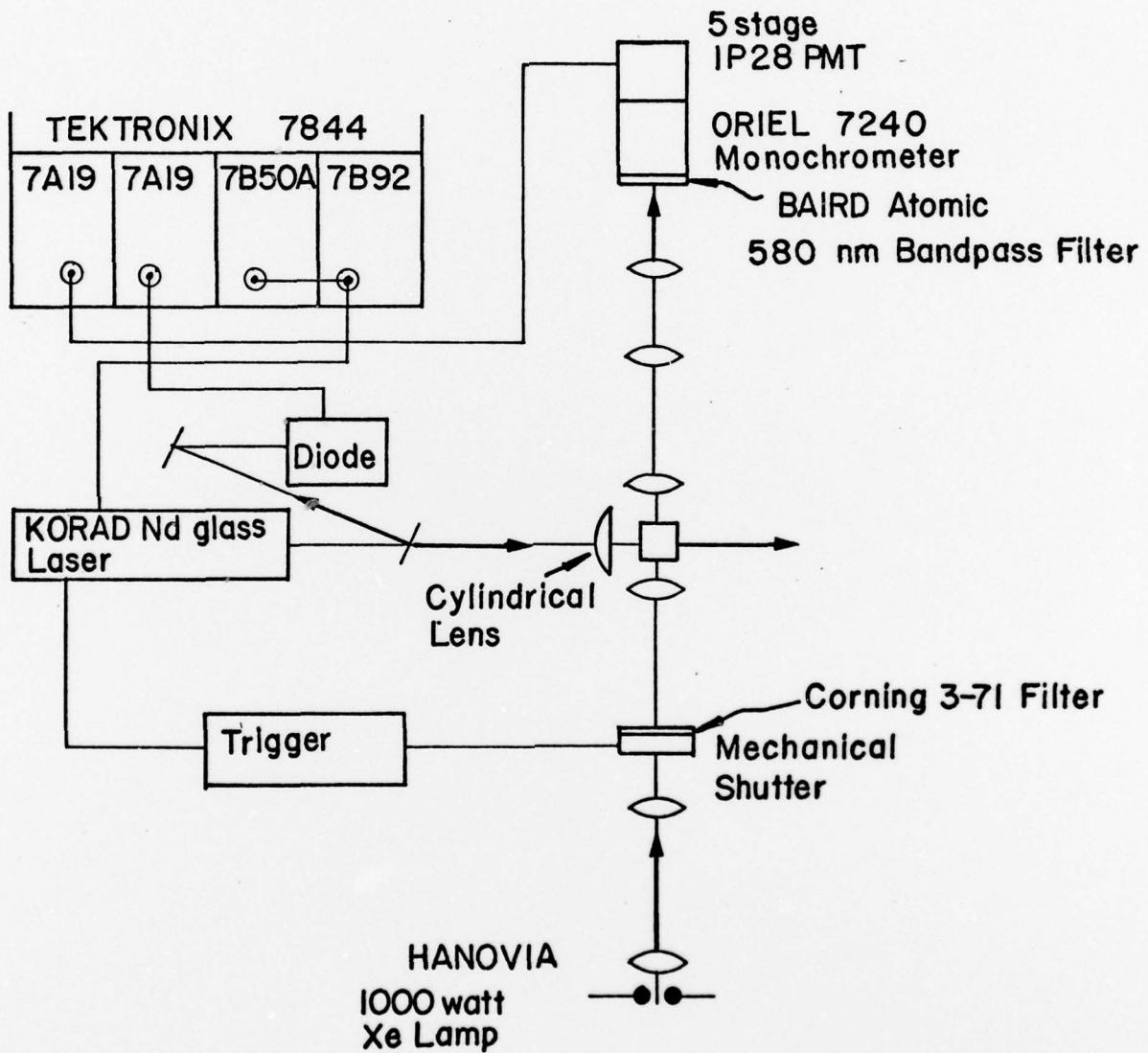


Fig. 3

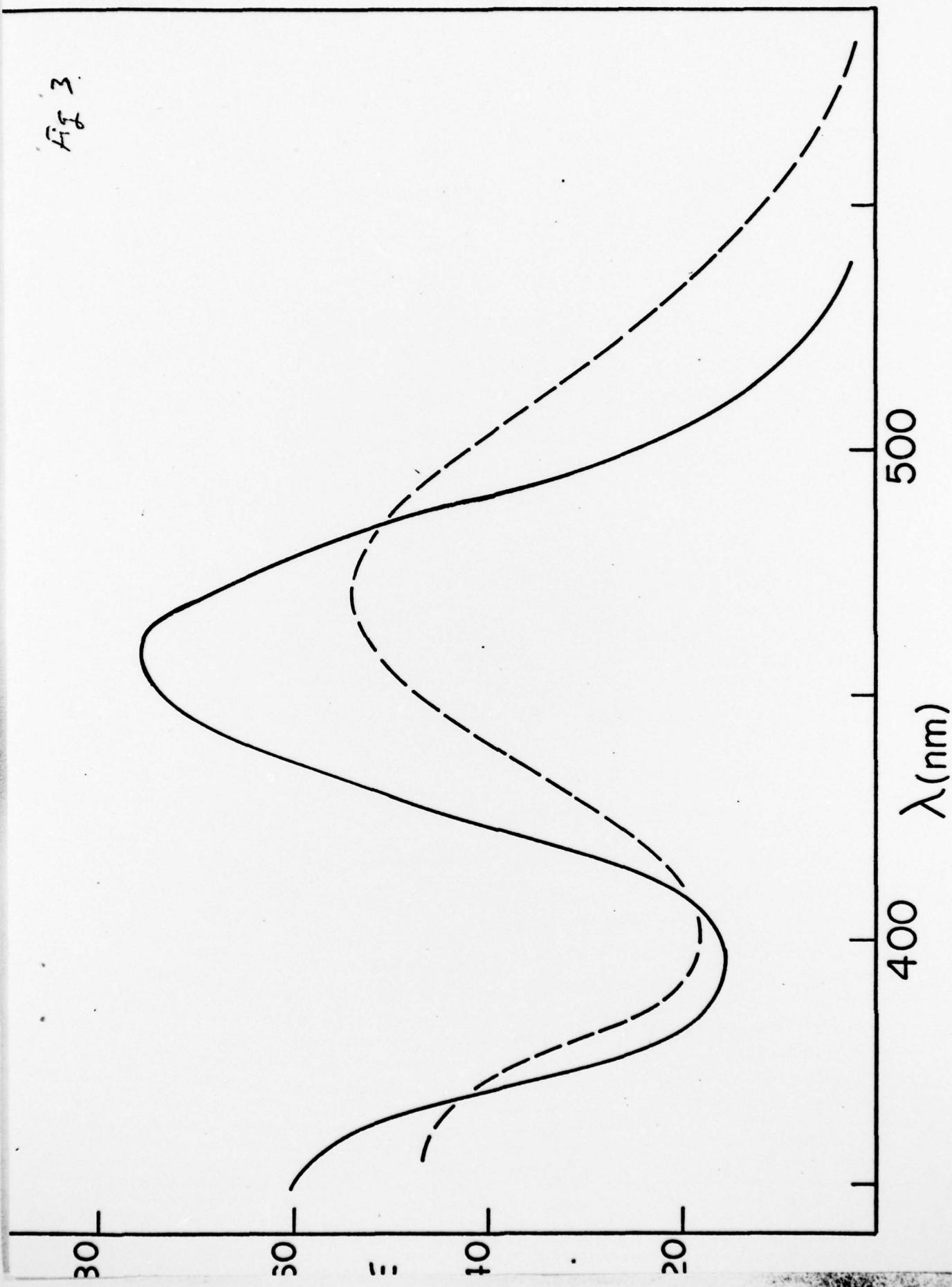


Fig. 4.

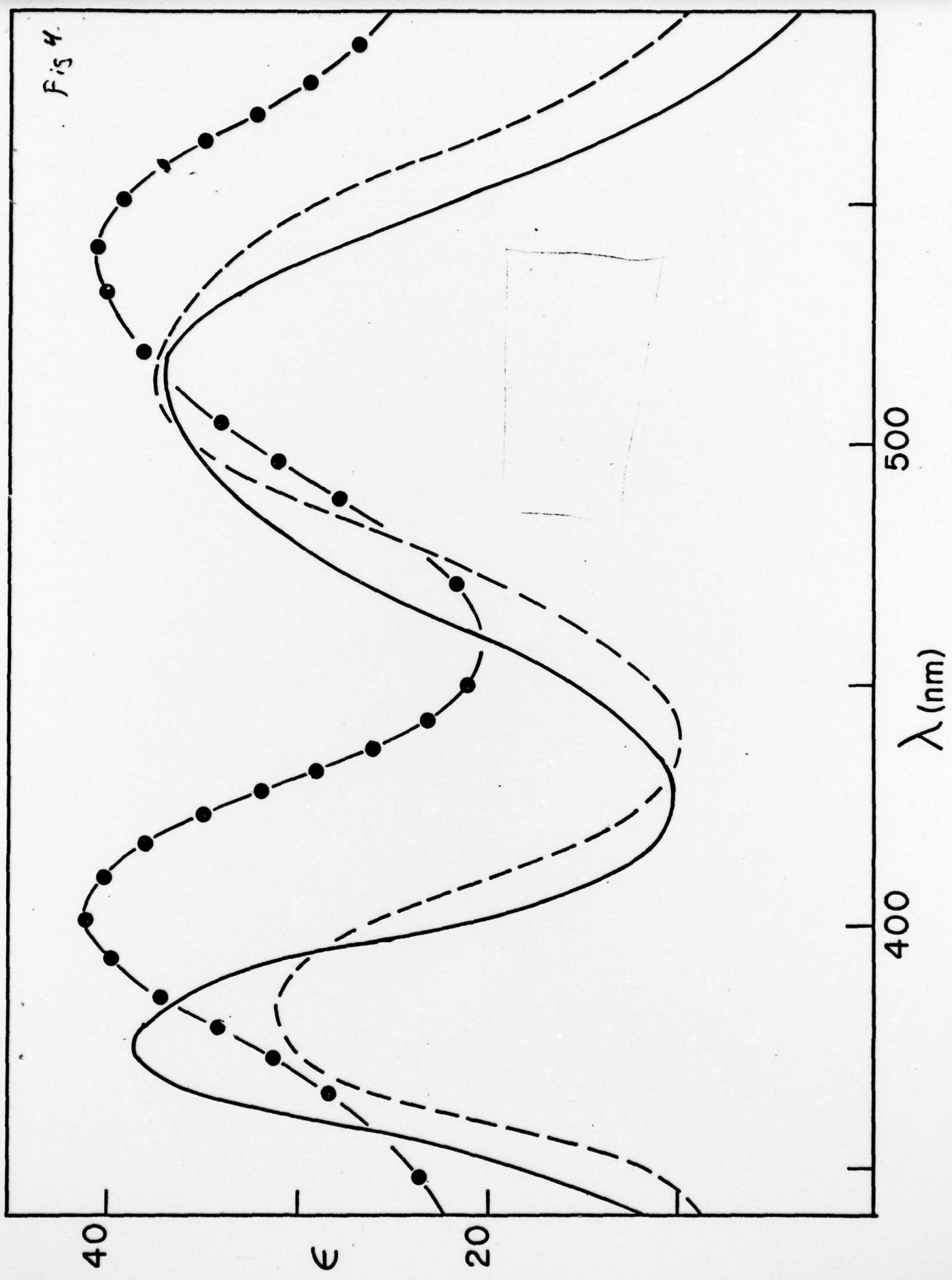
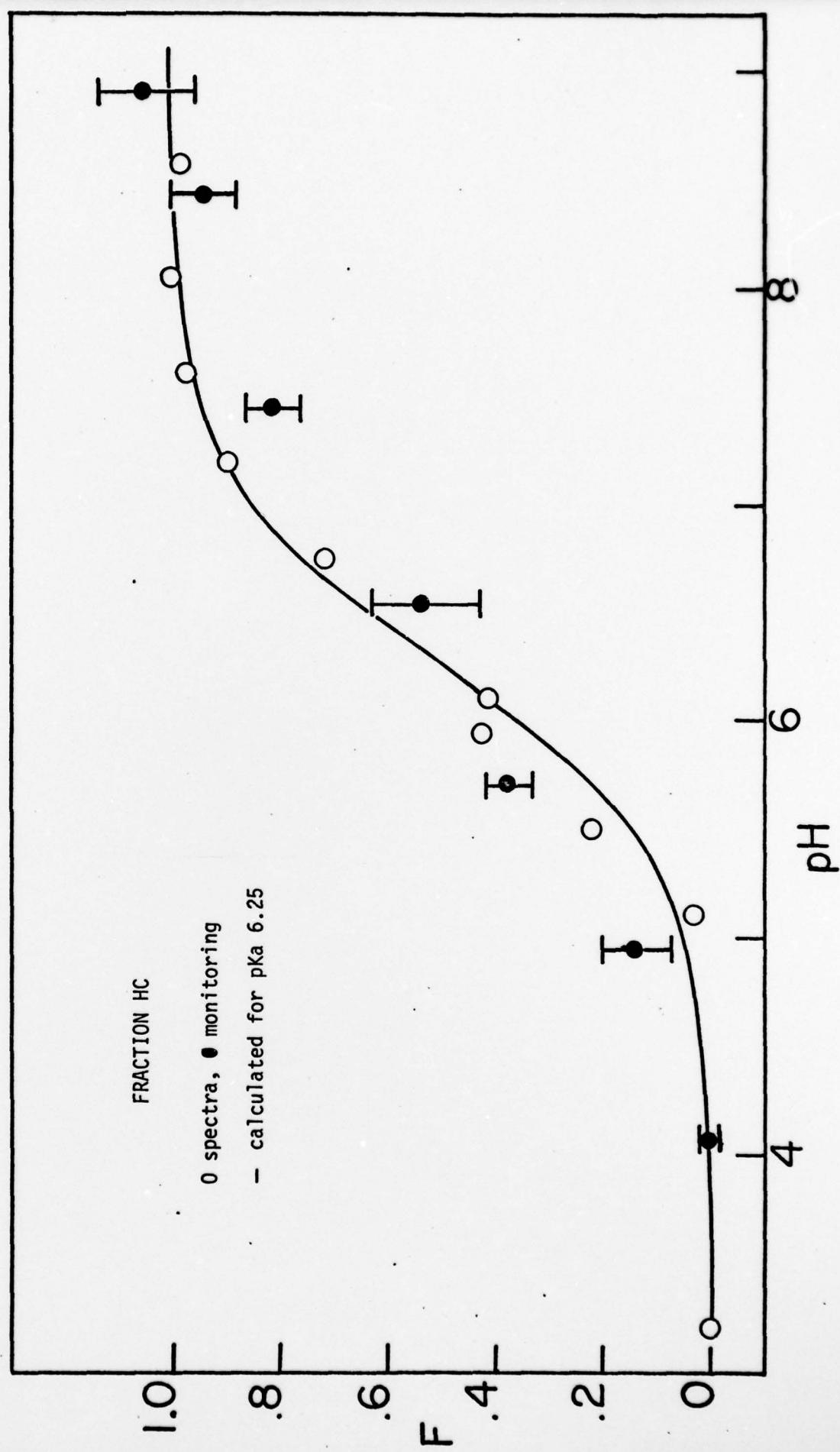


fig 5



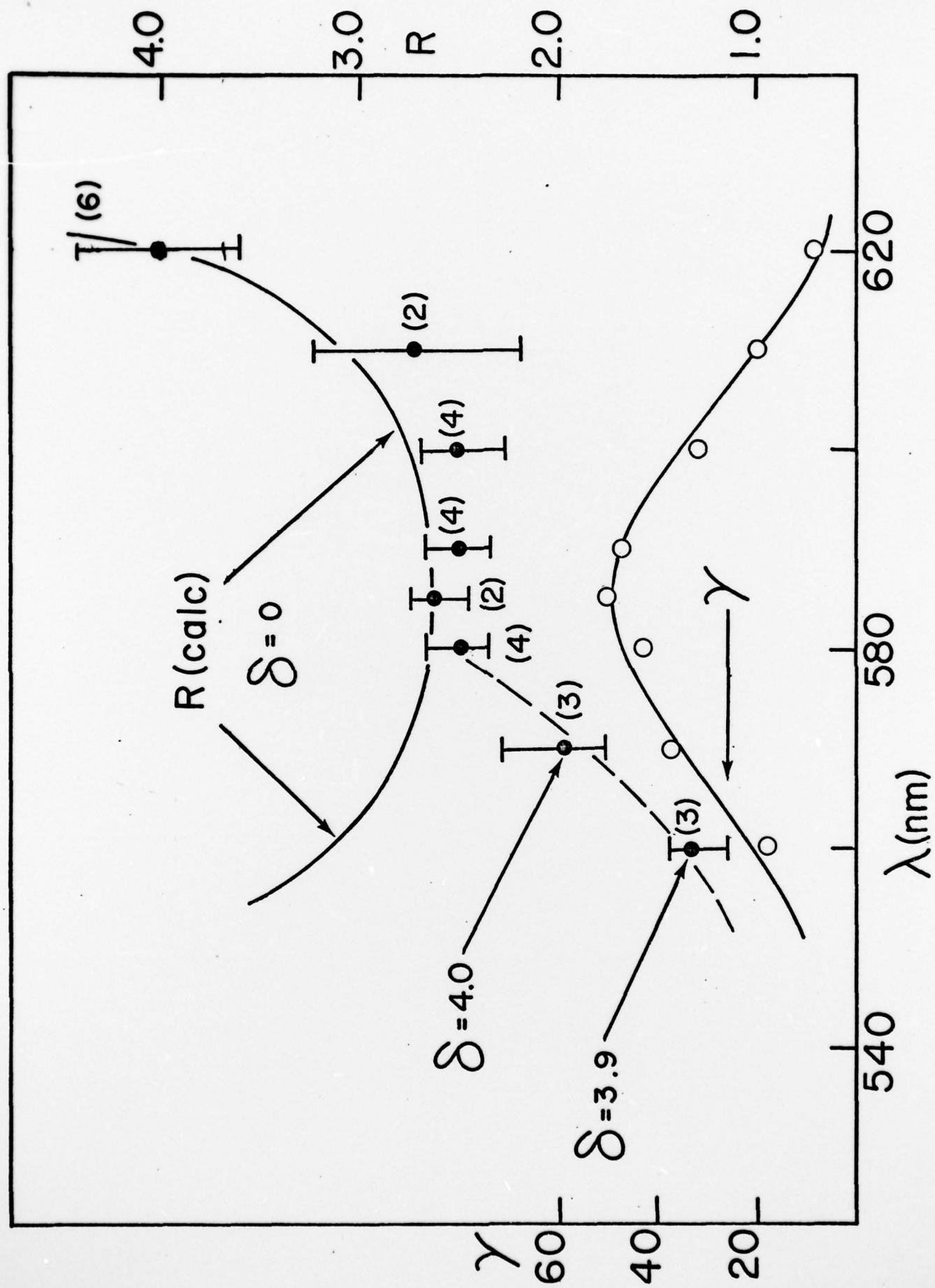
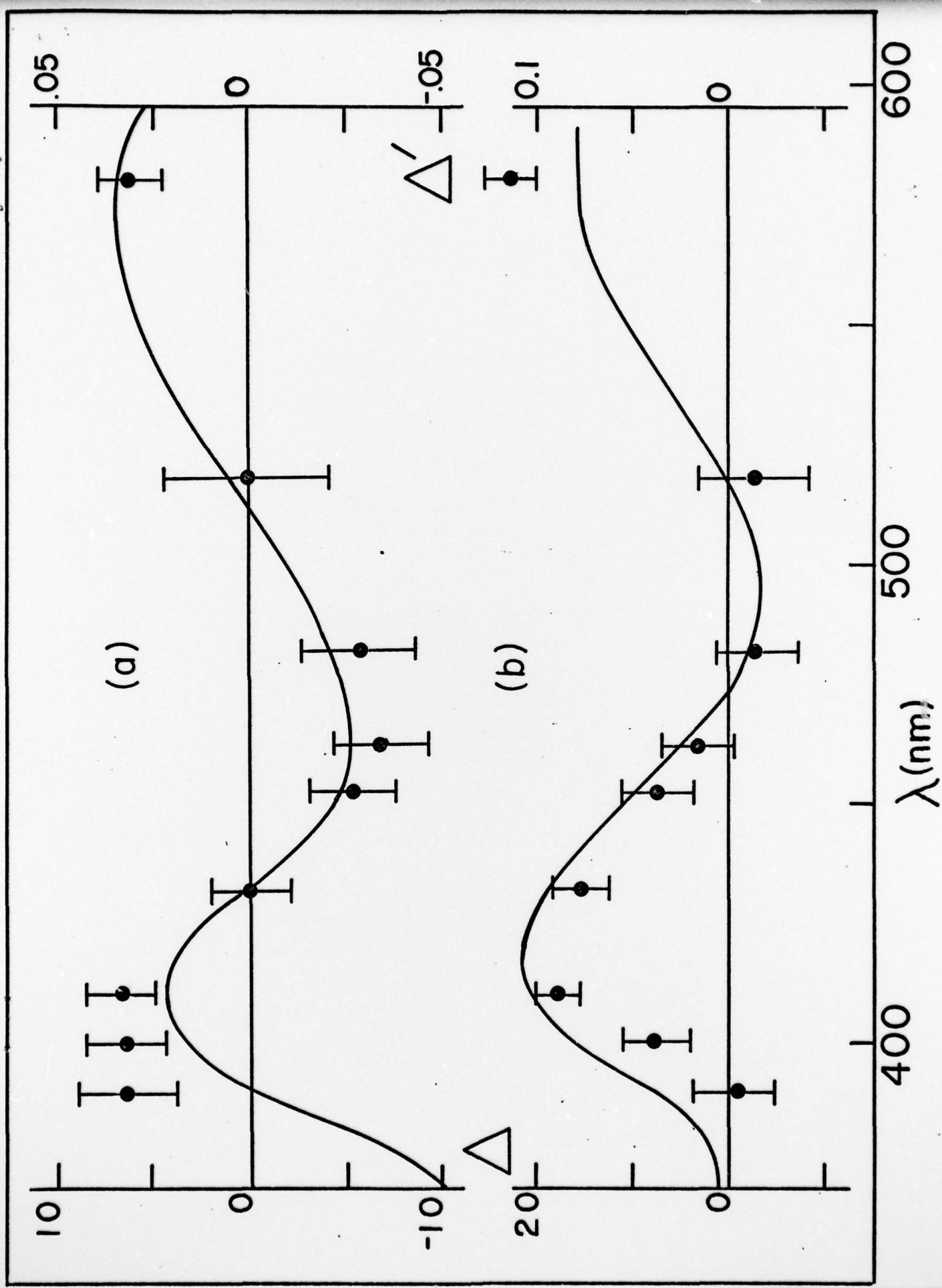


Fig. 7



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